



Review

A review: Feasibility of hydrogen generation from the reaction between aluminum and water for fuel cell applications

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H I G H L I G H T S

- ▶ Hydrogen generation from the reaction of aluminum with water were reviewed.
- ▶ Aluminum activated by various means were summarized in details.
- ▶ The effects of additives on the hydrogen generation characteristics were evaluated.
- ▶ Available hydrogen generators based on aluminum hydrolysis reaction were presented.

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Direct hydrogen fuel cell power system as an alternative of current batteries is promising for portable applications because of its potential better energy and power density. Straight feeding hydrogen, which is generated from a chemical reaction process, to a fuel cell system requires a load-response hydrogen generation rate which is generally not easy to obtain. Hydrogen generation from the reaction between aluminum and water offers a simple way to acquire hydrogen which can be directly fed to a fuel cell power system, however, the oxide film formed on the surface of aluminum particles will generally stop the reaction to proceed. In the present review, metal aluminum activated by various techniques, namely by the addition of alkaline solutions, carbon materials, oxides and by alloying with other elements, are summarized. The effects of the additives on the hydrogen generation characteristics are evaluated. The available hydrogen generators based on the reaction between aluminum and water are discussed and some recommendations for future work are also proposed.

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1. Introduction

The interest of developing hydrogen as an alternative of carbon-based fossil fuels arises from its potential environmental and energy-supply benefits. Firstly hydrogen can be used to generate electricity through fuel cells (FCs) or hydrogen internal combustion engines (ICEs), which can then be used to drive electronic devices, vehicles, home electric appliances and so on [1,2]. Hydrogen can also directly burn to produce heat for residential applications. Such a hydrogen utilization process is environmentally benign because it does not produce carbon emissions and thus a wide use of hydrogen “fuel” would significantly reduce the negative impact of

carbon emissions on environment [3,4]. It is generally recognized that the enormous carbon emissions caused by the use of fossil fuels on an increasing scale is the main reason for the global warming [5]. Secondly hydrogen is a versatile energy carrier that can be produced not only from a variety of primary energy sources including natural gas [6], coal [7], petroleum [8], and so on, but also from water electrolysis [9] or biomass [10]. The latter case is particularly important because it can seemly offer a solution for the issues of depletion of fossil fuels worldwide and degraded environment quality caused by the use of fossil fuels on a large scale, especially when the renewable energy is incorporated into its hydrogen production process. However, a wide use of hydrogen “fuel” is still facing many hindrances, namely lack of cost competent hydrogen generation techniques and efficient storage and transportation means [11].

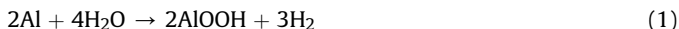
It is known that currently most industrial hydrogen is yielded from fossil resources through chemical methods, for example natural gas reformation [12]. These methods are neither eco-

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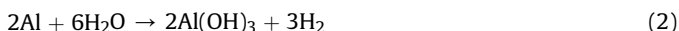
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friendly nor sustainable. Recently hydrogen generated from the reaction of aluminum or aluminum alloys with water becomes interesting because of its low cost, relatively high hydrogen storage capacity and simplicity of the hydrogen generation system. Such a hydrogen generation route is particularly suitable for portable fuel cell application. The aluminum hydrolysis reaction related to hydrogen generation is basically expressed as follows [8,13]:



or



According to reaction (1) or (2), 1245 cm³ of H₂ (N.T.P.) could be collected when 1 g Al completely reacts with water. The byproducts Al(OH)₃ or AlOOH are stable, non-corrosive and an important raw material for ceramic industry. This process is not involved in carbon emission. However it is well recognized that metal aluminum is prone to be oxidized and the passive oxide film covered on its surface would generally not allow reaction (1) or (2) to take place to produce hydrogen [13,14]. Therefore removing the passive oxide film or keeping aluminum or aluminum alloy in an activated state is essential to yield hydrogen by reaction (1) or (2) for practical fuel cell applications. Some techniques for example by mechanical polishing or cutting [15] have been used to eliminate the thin aluminum oxide layer allowing the hydrogen generation reaction to continue. Adding alkaline catalysts such as NaOH or KOH [16,17] is also proven to be effective in sustaining the hydrogen generation reaction between aluminum and water. Some studies have shown that doping some metal elements such as Bi [1,18], Sn [19], In [20], Ga [14,21], Mg [22], etc. into aluminum to form aluminum alloys could improve aluminum reactivity. Some oxides or carbon materials were also employed to improve the reactivity of aluminum [11,23–25].

In the present review, the existing activation methods for aluminum to produce hydrogen according to the reaction between aluminum or its alloys and water were summarized. The feasibility of hydrogen generation system for fuel cell applications, using reaction (1) or (2) as the hydrogen supplier, was evaluated. In addition, the future challenges for aluminum-based hydrogen generator, such as availability of activated aluminum materials, instant removal of hydrolysis product and heat removal, were also proposed.

2. Direct hydrogen fuel cell power system

Unlike widely used batteries, such as zinc–manganese dioxide (Zn–Mn) [26], lead acid [27], nickel metal hydride (Ni–MH) [28] and lithium-ion (Li-ion) [29–31] where the electrochemical energy is stored inside the batteries, a hydrogen fuel cell is only an electrochemical energy conversion device, as illustrated in Fig. 1 [32]. It works like an internal combustion engine and as long as it is fed by the hydrogen and oxygen “fuel” externally, the electricity including heat and water can be continuously generated from the fuel cell. Such a hydrogen fuel cell power system shows some merits over traditional ICEs, namely zero emission, high efficiency, low noise during operation and potential long running life time.

It is noted from Fig. 1 that hydrogen should be supplied to the anode side externally to generate electricity and obviously the purity, pressure and flow rate of hydrogen will play a vital role in determining the performance of the hydrogen fuel cell power system since oxygen is generally taken from air when the air breathing technique is employed. To obtain a required load-response hydrogen flow rate, the common solution is to add

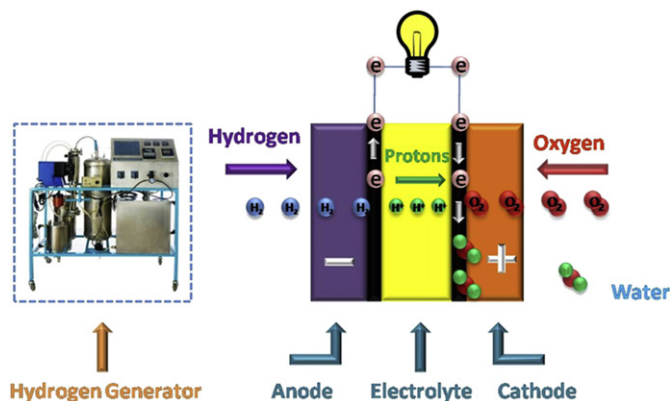


Fig. 1. Schematic diagram of direct hydrogen fuel cell power system [32].

a hydrogen buffer, either pressure tank [33] or metal hydride tank [34], between the hydrogen generator and fuel cell. However the incorporation of hydrogen buffer into the fuel cell power system would significantly lower the system compactness which is not feasible in most portable application cases. Therefore it is interesting to couple the hydrogen generator directly with fuel cell to obtain a compact power system for end users.

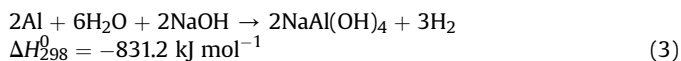
Considering the simplicity of the hydrogen generation reaction between metal aluminum and water, it may provide such a possibility of directly coupling Al-based hydrogen generator to a fuel cell and thus obtain a compact fuel cell power system. However metal aluminum should be activated first before such a power system becomes possible.

3. Activation of aluminum

As mentioned above, the hydrogen generation reaction (1) or (2) is easy to take place if the aluminum is kept in a fresh or activated state. However in most cases aluminum surfaces are covered by passive oxide layers which would stop the reaction to proceed. Many measures have been developed to remove the oxide layers, allowing the hydrogen generation reaction to progress.

3.1. Activated by alkaline

Alkaline is one kind of simple and low cost catalyst for aluminum hydrolysis reaction and thus placing aluminum in alkaline solutions provides a simple way to produce hydrogen. The reaction between aluminum and alkaline solution (e.g. NaOH) has been widely reported [8,16,17,35], which is expressed as follows (reaction (3)):



The added NaOH can be regenerated from the as-formed product NaAl(OH)₄ by temperature variation through reaction (4) and so the overall hydrogen generation reaction is similar to reaction (2).

Generally, hydrogen generation rates according to reaction (3) are dependent on temperature, alkali concentration and morphology of aluminum starting materials. Early in 1970s, Belitskus [36] discovered that sodium hydroxide solution was suitable for hydrogen generation by reacting with aluminum powder and the complete consumption of aluminum required at least 1.5 g

NaOH per gram of Al to attain a rapid hydrogen generation rate. Stockburger et al. [37] reported that to obtain the highest hydrogen production rate based on reaction (3) the suitable reaction temperature and NaOH concentration were determined as 343–363 K and 5.75 M NaOH respectively. Martinez et al. [35] have reported that using a glassware Kipp generator, consuming 100 aluminum soft drink cans could produce hydrogen with an amount equivalent to 5 kWh in a few hours. Subsequently [38], they tried to feed the hydrogen generated from the aluminum cans and NaOH solution to a PEM fuel cell to generate electricity. Jung et al. [39] designed a prototype microreactor for the reaction of aluminum powder and water using NaOH as the catalyst, which is targeted at portable fuel cell application. Hiraki et al. [40] developed an industrial-scale hydrogen generator system by which 1 kg H₂ with a pressure of 30 MPa was obtained using 60 kg waste Al and 18 kg water as the starting materials. In their report [41], a systematic evaluation by LCA (life circle assessment) showed that the proposed process which produces 1 kg of hydrogen and 26 kg of aluminum hydroxide from waste aluminum was only 2% in terms of energy requirement and 4% in terms of carbon dioxide emission in comparison to the conventional processes used for generation of hydrogen and formation of aluminum hydroxide. Soler et al. [42] studied the difference in hydrogen production rate by using various aluminum raw materials. It was found that aluminum in flake shape showed the lowest hydrogen generation rate because of its lower specific surface area than those in powder or foil states. Similar results were also observed by Aleksandrov et al. [16]. Besides the above parameters, the alloy composition and species also influence the hydrogen generation rate between alloys and caustic solutions. Hu et al. [43] determined that the higher proportion of Al in the Ni–Al alloy, the greater hydrogen generation rate in NaOH solution. Soler et al. [42] compared the reactivities of 16 tested type alloys in caustic solution. It was found that Al/Si alloys have the greatest reactivity. Yoo et al. [44] also studied the effect of Si content in Al–Si alloy powder with NaOH on H₂ production and the total amount of H₂ produced decreased as Si content increased.

In addition to NaOH, other hydroxides, such as KOH or Ca(OH)₂, were also used as the catalysts for hydrogen production. Soler et al. [17] carried out an experiment by aluminum corrosion using KOH solution as catalyst. The best hydrogen production conditions were found to be at 348 K and using a 5 M KOH solution. However, hydrogen generation rate is decreased with the reaction process due to the atmospheric carbonation of KOH solution to produce potassium hydrogen carbonate. In a later investigation [42], they reported that the addition of a mixed KOH and NaOH solution showed a synergistic effect in increasing hydrogen generation rate,

but aluminum corrosion was always faster by using NaOH instead of KOH at the same concentration and temperature. Jung et al. [39] developed a flow-type reactor in which aluminum pellet combined with CaO was put into NaOH solutions to produce hydrogen. The combination of CaO and NaOH is more efficient in obtaining the maximum conversion of aluminum and the maximum conversion of 78.6% is achieved. Recently Pudukudy et al. [45] reported that when a mixed CaO and NaCl was used as an additive, an enhanced corrosion rate of Al foil and total amount of H₂ generated in sea water were obtained. The results of some typical studies on hydrogen production via the reaction of Al or Al alloys in alkaline solutions are summarized in Table 1.

The mechanism of the enhanced Al corrosion in alkaline solution is easy to understand [46,47]. The provided OH[−] can dissolve the protective oxide film formed on the surface of aluminum by a chemical attack progress, leading to the presence of the fresh Al surface which would react with alkaline solution to produce aluminate ion Al(OH)₄[−] and H₂. Obviously, the dissolution rate of the protective oxide film would be influenced by the concentrations of OH[−] provided, i.e., the hydrogen generation rate will be dependent on the alkaline concentrations, as observed.

3.2. Activated by oxide additives

Though caustic solutions can enhance the hydrogen generation reaction between aluminum and water, its corrosive nature limits its applications. Allowing the hydrogen generation reaction (1) or (2) to take place at ambient temperature and to use pure water rather than caustic solution is greatly preferred for engineers to design a simple generator. To obtain aluminum materials with a high reactivity, some oxide additives were employed to improve the hydrolysis reactivity of aluminum in water. Chaklader [48,49] investigated the hydrogen generation characteristic of the aluminum–aluminum oxide or hydroxide composite powders. In his work, bayerite (Al(OH)₃), boehmite (AlOOH), alpha-alumina (α-Al₂O₃) or gamma-alumina (γ-Al₂O₃) were added into aluminum powder to form an aluminum–aluminum oxide or hydroxide composite powders by a mechanical milling processing. It was found that the presence of aluminum oxide or hydroxide could enhance the hydrogen generation reaction of aluminum and the maximum hydrogen evolution was attained when α-Al₂O₃ powders were added.

Deng et al. [50,51] used a ceramic processing to prepare aluminum oxide or hydroxide modified Al composite particles. In their experiments, the aluminum oxide or hydroxide modified Al composite particles were prepared by ball milling the mixture of Al and Al(OH)₃ powder in an ethanol solution, and then dried

Table 1
Typical results on hydrogen production via the reaction of Al or Al alloys in alkaline solutions.

Metal/Metal alloys	Reaction solution	Reaction temperature (K)	Maximum hydrogen generation rate	Maximum hydrogen conversion yield	Ref
Al foil/powder	NaOH	287–353	40 cm ³ s ^{−1} cm ^{−2} for Al foil 6.3 cm ³ s ^{−1} g ^{−1} for Al powder	–	[16]
Al foil	KOH	343–353	260 cm ³ min ^{−1}	–	[17]
Al powder	NaOH	322.7–357.5	–	78.6% for Al–CaO mixture (weight ratio = 0.3:1) + NaOH (5 wt.%)	[39]
Al–CaO	NaOH	291.2–333.2	–	100% (T > 313 K)	[41]
Al powder	NaOH	298–348	216 cm ³ min ^{−1} g ^{−1} for Al 88/Si 12 alloy	76% for Al 88/Si 12 alloy	[42]
Al alloys	NaOH, KOH, Ca(OH) ₂	–	–	–	–
Al–Ni alloys	NaOH	293–333	–	>95%	[43]
Al foil/CaO/NaCl	Sea water	298–333	–	100% for Al–[sea water (20 cm ³) + CaO (3 g) + NaCl (0.15 g)]	[45]

followed by calcining in a vacuum furnace at 873 K. It was found that the as-prepared aluminum-based composite powder could continuously react with water at room temperature until all the aluminum powders were consumed. Recently, they [11] extended their work by using different oxides (γ - Al_2O_3 , α - Al_2O_3 , TiO_2) to modify the surfaces of Al particles. They found that γ - Al_2O_3 showed a better effect in improving the reactivity of aluminum than α - Al_2O_3 or TiO_2 . Skrovan et al. [52] also found that corrosion rate of aluminum powder in water is dependent on the amount of Al_2O_3 added. When the Al_2O_3 quantity was increased during milling, a larger surface area of aluminum was obtained, which results in a higher corrosion rate of aluminum in water. Based on their observations, Deng et al. [53] proposed a physicochemical model to explain the favorable effect of Al_2O_3 additive on the hydrogen evolution of aluminum in water, as illustrated in Fig. 2. A thin Al_2O_3 film covering on the surface of aluminum particles would be formed during the milling process by the addition of Al_2O_3 . When such an Al_2O_3 -modified Al particle is put into water, the Al_2O_3 film

on the surface would be hydrated to form a boehmite ($\text{Al}(\text{OH})_3$) layer, which would further grow by the OH^- transport in the film. When the hydrated front meets the metal Al surface, OH^- ions would react with Al and form H_2 bubbles at the Al/ Al_2O_3 interface. When the reaction equilibrium pressure in H_2 bubbles exceeds a critical gas pressure that the hydrated oxide film can sustain, these bubbles would then rupture the Al_2O_3 layer, leading to the activation of aluminum.

Except for Al_2O_3 additive, other oxides such as TiO_2 , Co_3O_4 , Cr_2O_3 , MoO_3 , Bi_2O_3 , CuO [23,24] etc. were also employed to improve the hydrolysis reactivity of aluminum. Compared with Co_3O_4 and Cr_2O_3 nanocrystals, Wang et al. [23] found that TiO_2 nanocrystals exhibited the most pronounced effect in improving the reactivity of aluminum either in deionized water or in tap water. Pitting is proposed as the major reason for the improvement in reactivity of aluminum in the Al/ TiO_2 composite. Dupiano et al. [24] also observed the similar effect by the addition of MoO_3 , Bi_2O_3 , CuO into Al through the mechanical mixing. An enhanced hydrogen evolution rate and complete reaction of aluminum were observed for the Al/ Bi_2O_3 composite powder. A “modified protective interface” concept, similar to Deng’s model [53], was also proposed to explain such an improvement.

Comparing with the hydrogen generation by putting Al in caustic solutions, hydrogen generation by hydrolysis of the aluminum powder modified by oxides is more feasible for portable fuel cell applications because it can be carried out at ambient temperature and pure water. This would simplify the system and be easy to control the reaction. However, obtaining and/or maintaining a sufficient hydrogen evolution rate remains a big challenge for system designers [8,12].

3.3. Activated by carbon materials

Carbon material, such as graphite, is a common anode material that is widely used in Li-ions batteries [54,55]. Some attempts have been also tried to use carbon materials to improve the hydrolysis reactivity of aluminum. Chaklader [49] reported that lampblack carbon is an effective additive for Al/C system in generating hydrogen from water. The maximum hydrogen generation volume of $738 \text{ cm}^3 \text{ g}^{-1}$ of Al was obtained for the Al/C composite containing 60 wt.% carbon. Streletskii et al. [56] also observed the enhanced aluminum hydrolysis activity by addition of 10–30 wt.% graphite, which was attributed to the formation of aluminum carbide phase during the high speed milling process. Recently Huang et al. [25] found the improvement of Al hydrolysis reactivity by the addition of graphite. They prepared the aluminum/graphite composite by a ball milling process which formed a core-shell structure. As shown in Fig. 3, the hydrogen evolution of the as-prepared aluminum/graphite composite is increased with the increased amount of graphite. No remarked hydrogen evolution is detected for the sample without addition of graphite. As containing 23 wt.% graphite, 76.5% Al can react with water to yield hydrogen in 6 h. The final 80.1% of conversion yield is obtained for the sample containing 43 wt.% graphite.

In addition to graphite, other non-oxide materials such as SiC were also used as modifiers for hydrogen production [13]. Czech and Troczynski [13] found that SiC was an effective additive in improving the reactivity of aluminum. The amount of generated hydrogen attained $380 \text{ cm}^3 \text{ g}^{-1}$ of Al when the Al/SiC composite was put into 328 K water.

3.4. Activated by amalgam

The amalgamated aluminum usually works as aluminum alloy anodes, which are widely used in both batteries and sacrificial

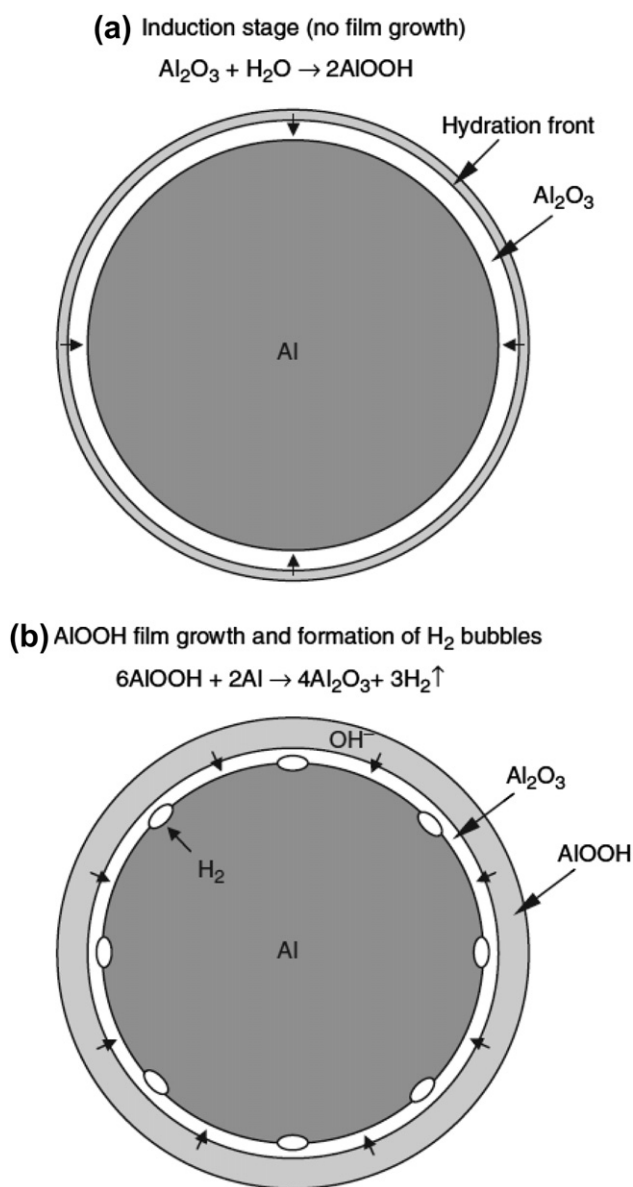


Fig. 2. Schematic diagram of the hydration reaction inside the passive oxide film on the Al particle surface: (a) induction stage in which no film growth occurs; (b) $\text{Al}(\text{OH})_3$ film growth and formation of H_2 bubbles. Taken from Ref. [53].

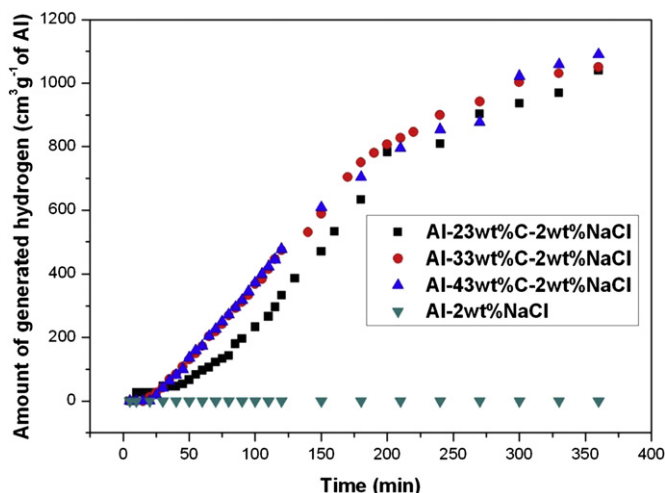
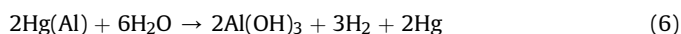


Fig. 3. Effect of graphite additive on the hydrolysis reaction between the Al/C composites and water. Taken from Ref. [25].

protection [57,58]. Amalgam can also be used to induce aluminum hydrolysis reaction though it is generally toxic. Early in 1889, Cohen and Ormondy [59,60] found that an amalgamated aluminum surface could react with water, producing aluminum hydroxide and hydrogen. Later in 1972, Smith [61] designed a hydrogen generation system based on the reaction between amalgamated aluminum and water. It was found that the hydrogen generation reaction rate was strongly dependent on the reaction temperature. The amalgam types also influenced the generation reaction rate [62]. Zinc amalgam was found to show the biggest effect in improving the aluminum hydrolysis reaction [62]. Recently Huang et al. [63] also reported that maximum hydrogen generation rate of $43.5 \text{ cm}^3 \text{ h}^{-1} \text{ cm}^{-2}$ was obtained at 338 K for the aluminum coated with zinc amalgam, which is three times higher than that in the case coated with mercury ($13.7 \text{ cm}^3 \text{ h}^{-1} \text{ cm}^{-2}$). This was generally attributed to the lower surface free energy of the ternary aluminum–zinc–mercury alloy than the binary aluminum–mercury alloy.

The corruptions of aluminum by mercury or amalgam have widely been observed [58,64–66] and the mechanism for such corruptions is generally attributed to a combination of physic and electrochemical process [67]. The first process of physical corrosion refers to amalgamation. Mercury adsorption on bare Al induced localized reduction in the strength of the atomic bonds of Al. An amalgam is formed on the aluminum surface when mercury enters into a metallic aluminum. The second step is electrochemical corrosion. It represents for the electrochemical oxidation of Al and water reduction [58]. The activated aluminum ion from the second step can come out from the amalgam and react with water to produce hydrogen. The whole hydrolysis reaction induced by mercury or amalgam is generally described as follows:



Recently Huang et al. [63] confirmed that when the mercury was put on the aluminum surface, some fresh aluminum points or area would react with mercury first to form corrosion pits and then these corrosion pits will propagate to other area due to the induced stresses, leading to the breakdown of the oxide film. When the aluminum species in mercury move to the mercury/water interface, they would react with water quickly to generate hydrogen due to their high reactivity. The aluminum is continuously dissolved in the

mercury and then transported to the mercury/water interface sustaining the hydrogen generation to proceed. Such a process is illustrated in Fig. 4.

3.5. Activated by doping with other metal elements

Al doped with other metals (Ga, Bi, Sn, In, Ni, etc.) to form Al-based alloys is an important way to acquire high Al hydrolysis reactivity in water. Melting and mechanical ball milling are generally used to prepare Al-based alloys. Kravchenko et al. [21] used a melting processing to prepare the Al-based alloys containing Ga, In, Zn and Sn and found that Al-based alloys showed a higher reactivity over metal aluminum and produced hydrogen $1000 \text{ cm}^3 \text{ g}^{-1}$ of Al in pure water at 355 K. The improved reactivity of aluminum was ascribed to the liquid eutectic effect of Al with other metals, where other metals such as gallium would penetrate into aluminum grain boundaries, break intercrystal contacts and form aluminum monocrystal particles covered by eutectic thin film, and thus speed up its hydrolysis reaction with water [14]. Wang et al. [64] also prepared Al–Ga–In–Sn alloys by an arc melting processing. They proposed a mechanism to account for the observed high reactivity of Al. The nanosized Al species with high reactivity would transport through Ga–In–Sn to the reaction sites to generate hydrogen at the initial stage. The convection or agitation caused by the reaction swept away the hydroxide layer formed on the fresh Al surface and promote the reaction continuously until all the Al powders were consumed.

Compared with melting processing, ball milling is another simple processing to synthesize Al-based alloys containing other metals [68]. Fan et al. [1,18,20,68–70] have reported that mechanical alloying is feasible to synthesize Al-based alloys for hydrogen production. In his work, different metals such as Zn, Ca, Ga, Bi, Mg, In, Sn, Hg, Li, etc. were used as the dopants in an attempt to improve the reactivity of Al. The enhanced reactivity of Al-based alloys in pure water was predominately ascribed to the formation of galvanic cells after having immersed the alloy powders in water. On the other hand, the increased amounts of surface defects and grain boundaries formed during the milling progress would also contribute to the improved Al reactivity.

3.6. Activated by other additives

It has been well documented that water soluble inorganic salts can produce localized pitting and rupture of the alumina layer on aluminum particles and thus increasing the reactivity of Al in water [71,72]. Such effects have been employed to promote aluminum–water hydrogen production reactions. Alinejad and Mahmoodi [73] studied the effect of NaCl additive on hydrogen generation by hydrolysis of Al–NaCl ball-milled materials. It was found that increasing the mole ratio of salt to aluminum resulted in decrease of aluminum particle size, which led to an improvement in reaction kinetics and formation of salt gates in aluminum particles. These

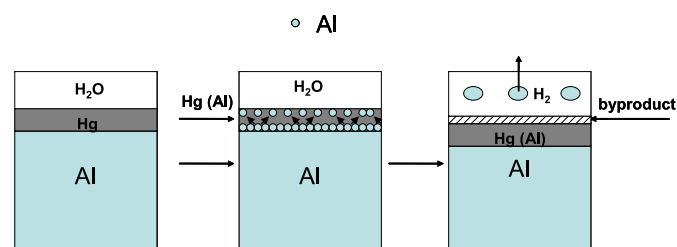
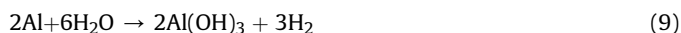


Fig. 4. Schematic diagram of proposed aluminum hydrolysis model induced by mercury. Taken from Ref. [63].

gates were washed away when the mixed powder was put in water so that the hydrolysis reaction took place easily. For the powder with salt to aluminum mole ratio of 1.5, the highest hydrogen generation rate and hydrogen yield reached to be $75 \text{ cm}^3 \text{ min}^{-1}$ and 100%, respectively. In a recent study [74] they further identified that Al–NaCl powder showed an excellent capability for long-term storage in air. The powder with salt to aluminum mole ratio of 2 generated hydrogen with 100% efficiency after being stored in the air for two months. Czech and Troczynski [13] discussed the corrosion rate of aluminum powder milled with different salts in a 1:1 weight ratio. Higher hydrogen generation rates and total hydrogen generation volumes were obtained when using KCl instead of NaCl. Fan et al. [1] investigated the effect of different salts (KCl, NaCl, LiCl, MgCl_2 , AlCl_3) on the reactivity of Al–Bi alloys in water. MgCl_2 addition showed a better effect in improving the reactivity of Al over other salts due to its high dissolution enthalpy. The results of hydrogen production by hydrolysis of the Al powders milled with salts are summarized in Table 2.

Except inorganic salts, sodium borohydride (NaBH_4) was also used to improve the reactivity of Al. Shafirovich et al. [75] found the Al/ NaBH_4 mixture with optimized mass ratio could supply stable hydrogen generation with about 7 wt.% yield. A synergistic effect has been observed in hydrogen production rates and yields combining Al or Al alloys with NaBH_4 in aqueous solutions [76]. The pH increase with the addition of NaBH_4 and the catalytic effects of some Al alloys are believed to be the main reason for the observed improvement of Al reactivity. Dai et al. [77] demonstrated that the $\text{NaBH}_4/\text{Al}/\text{NaOH}$ solid powder, in combination with the aqueous solution of CoCl_2 , constituted a high-performance hydrogen generation system. The hydrogen generation could be readily controlled by regulating the amount and rate of CoCl_2 solution into the $\text{NaBH}_4/\text{Al}/\text{NaOH}$ powder. Fan et al. [78–80] also confirmed that the addition of NiCl_2 or CoCl_2 had some catalytic effects on the hydrolysis reaction between Al–Li alloy with NaBH_4 mixture and water.

Soler et al. [81] obtained hydrogen from water using aluminum in sodium aluminate (NaAlO_2) solutions. It was found that the maximum rates and hydrogen production yields were improved when NaAlO_2 was used instead of NaOH in aqueous solutions. 100% of yield was achieved using NaAlO_2 concentrations higher than 0.65 M. The mechanism of Al corrosion in NaAlO_2 aqueous solutions is proposed as follows:



The passive oxide film would be hydrated to form $\text{Al}(\text{OH})_3$ on the aluminum surface (reaction (7)). AlO_2^{-1} act as a nuclei for $\text{Al}(\text{OH})_3$

crystallization, thus competing with $\text{Al}(\text{OH})_3$ precipitation process on Al surface. With the dissolution of $\text{Al}(\text{OH})_3$ (reaction (8)), the fresh aluminum surface would appear, allowing the reaction (9) to proceed. In another report [71] they further confirmed that a mixture of NaAlO_2 and $\text{Al}(\text{OH})_3$ exhibited a remarked synergistic effect on Al corrosion in distilled water. A high hydrogen evolution rate of $1200 \text{ cm}^3 \text{ min}^{-1}$ and 100% conversion of Al were obtained within 2 min by using 0.49 M NaAlO_2 and 40 g dm^{-3} $\text{Al}(\text{OH})_3$.

A recent study [82] showed that the formation of microgalvanic cells allowed a faster production of H_2 in Al corrosion system using Na_2SnO_3 aqueous solutions in comparison to NaOH and NaAlO_2 . The microgalvanic cell was formed between the surfaces of Al and Sn micro particles that were reduced from Na_2SnO_3 . Ma et al. [83] discovered that a combined usage of NaOH and Na_2SnO_3 additives could dramatically improve the hydrogen generation kinetics of Al/ H_2O system. The system could complete a 100% fuel conversion with a maximum hydrogen generation rate of $2100 \text{ cm}^3 \text{ min}^{-1}$. Table 3 lists the results of some typical studies on hydrogen generation via the reaction of Al powder in aqueous solutions.

4. Hydrogen generation system

Recently several hydrogen generators based on aluminum hydrolysis reaction have been developed, using sodium hydroxide as a catalyst. Martinez et al. [35] built a glassware Kipp generator, using aluminum soft drink cans and sodium hydroxide solution as the starting materials to generate hydrogen. Subsequently [38], they tried to directly feed the hydrogen to a PEM fuel cell to generate electricity. Jung et al. [39] designed a prototype hydrogen generator based on the reaction of aluminum powder and water using NaOH as the catalyst. In their work, a microreactor was designed to accommodate the hydrogen generation reaction. Such a system is targeted at portable fuel cell application. Hiraki et al. [40] developed an industrial-scale hydrogen generator system using waste Al and distilled water as the starting materials. During the operation, the metal aluminum and distilled water were placed in a reactor (autoclave) and distilled water was compressed to a high water pressure level by a liquid pump to obtain a high hydrogen delivery pressure. The sodium hydroxide solution was then injected into the reactor to promote the hydrogen generation reaction. A hydrogen delivery pressure of as high as 30 MPa was obtained by such a generator using 60 kg waste Al and 18 kg water as the starting materials. It was also found that the concentration of sodium hydroxide solution plays an important role in the hydrogen generation reaction. When 5.0 M sodium hydroxide solution was used, a rapid and large reaction degree can be acquired.

Following the Kipp generator mechanism, Andersen and Andersen [84] designed a hydrogen generator based on reaction (3). The generator includes an expandable container where the pressure and temperature of the reaction causes the container to expand and contract to control the degree of immersion of an

Table 2
Typical results on hydrogen production by hydrolysis of the Al powders milled with salts.

Metal/metal alloys	Reaction solution	Reaction temperature (K)	Maximum hydrogen generation rate	Maximum hydrogen conversion yield	Ref
Al–Bi–(LiCl, NaCl, KCl, AlCl_3 , MgCl_2)	Water	Room temperature	$1050 \text{ cm}^3 \text{ g}^{-1}$ for Al–10 wt.% Bi–10 wt.% MgCl_2 in 5 min	93.4 wt.% for Al–10 wt.% Bi–10 wt.% MgCl_2	[1]
Al–KCl, Al–NaCl	Water	295–373	$450 \text{ cm}^3 \text{ min}^{-1} \text{ g}^{-1}$ of Al	100% for Al–50 wt.% KCl 71% for Al–50 wt.% NaCl	[13]
Al powder	$\text{Al}(\text{OH})_3$, NaAlO_2 , NaCl	348	$235 \text{ cm}^3 \text{ min}^{-1} \text{ g}^{-1}$ of Al for Al–[$\text{Al}(\text{OH})_3$ + NaAlO_2 (0.01 M) + NaCl (35 g dm^{-3})]	100% for Al–[$\text{Al}(\text{OH})_3$ + NaAlO_2 (0.01 M) + NaCl (35 g dm^{-3})]	[71]
Al–NaCl	Water	343	$75 \text{ cm}^3 \text{ min}^{-1}$ for Al–NaCl (mole ratio = 1:1.5)	100% for Al–NaCl (mole ratio = 1:1.5)	[73]
Al–NaCl	Water	328–363	–	100% for Al–NaCl (mole ratio = 1:1.5–1:7)	[74]

Table 3

Typical results on hydrogen generation via the reaction of Al powder in aqueous solutions.

Metal/metal alloys	Reaction solution	Reaction temperature (K)	Maximum hydrogen generation rate	Maximum hydrogen conversion yield	Ref
Al powder	NaOH, NaAlO ₂ , NaCl	348	1200 cm ³ min ⁻¹ for Al–[NaAlO ₂ (0.49 M) + Al(OH) ₃ (40 g dm ⁻³)]	100% for Al–[NaAlO ₂ (0.49 M) + Al(OH) ₃ (40 g dm ⁻³)]	[71]
Al flake/powder	Ca(OH) ₂ , NaBH ₄	348	190 cm ³ min ⁻¹ g ⁻¹ for Al/Si + NaBH ₄ combination in saturated Ca(OH) ₂	94% for Al/Si + NaBH ₄ combination in saturated Ca(OH) ₂	[76]
Al alloys	CoCl ₂	Room temperature	4.8 dm ³ min ⁻¹ for 1.0 g NaBH ₄ (s)/0.5 g Al/0.10 g NaOH/3.0 g 5 wt.% CoCl ₂ solution	91% for 1.0 g NaBH ₄ (s)/0.5 g Al/0.10 g NaOH/3.0 g 5 wt.% CoCl ₂ solution	[77]
NaBH ₄ /Al/NaOH	Water	303–333	206 cm ³ min ⁻¹ for 1 g of Al–10 wt.% Li–11 wt.% CoCl ₂ /NaBH ₄ mixture (weight ratio = 1:1)	100% for 1 g of Al–10 wt.% Li–11 wt.% CoCl ₂ /NaBH ₄ mixture (weight ratio = 1:1)	[78]
Al–Li–NiCl ₂ /NaBH ₄	Water	313–343	1778 cm ³ for 1 g of Al–10 wt.% Li–15 wt.% NiCl ₂ /NaBH ₄ mixture (weight ratio = 1:1) in 50 min	100% for 1 g of Al–10 wt.% Li–15 wt.% NiCl ₂ /NaBH ₄ mixture (weight ratio = 1:1)	[80]
Al powder/flake	NaOH, NaAlO ₂	338–358	204 cm ³ min ⁻¹ for Al–NaOH (0.1 M)	100% for Al–NaOH (0.1 M)	[81]
Al powder	NaOH, NaAlO ₂	293–348	337 cm ³ min ⁻¹ for Al–NaAlO ₂ (2 M)	100% for Al–NaAlO ₂ (2 M)	[82]
Al powder	NaOH, NaAlO ₂ , NaSnO ₃	293–348	1200 cm ³ min ⁻¹ for Al (1 g)–Na ₂ SnO ₃ (0.1 M)	71% for Al (1 g)–Na ₂ SnO ₃ (0.1 M)	[82]
Al/NaOH/Na ₂ SnO ₃	Water	Room temperature	2100 cm ³ min ⁻¹ g ⁻¹ Al for Al (1 g)–NaOH (0.2 g)–Na ₂ SnO ₃ (0.1 g)–H ₂ O (5 g) composite	100% for Al (1 g)–NaOH (0.2 g)–Na ₂ SnO ₃ (0.1 g)–H ₂ O (5 g) composite	[83]

aluminum fuel cartridge in water and consequently to control the intensity and duration of the hydrogen generation reaction.

To better control the hydrogen generation of reaction (3), Huang et al. [85] proposed an aluminum slurry concept to design the hydrogen generator. The concept behind the use of aluminum slurry is that it would allow the feeding of aluminum amount to become pumpable and controllable, which makes it possible to obtain a hydrogen flow rate on demand. Using appropriate dispersant and surface active agent, a stable aluminum aqueous slurry was prepared. The stoichiometric aluminum slurry and aqueous sodium hydroxide solution according to reaction (3) were fed into a reactor using two metering pumps, which can accept load signals and thus the hydrogen generation rate is controllable and load response. The generator is shown in Fig. 5(a) [86]. Such a generator can deliver a constant hydrogen flow rate of as high as 20 dm³ min⁻¹, as shown in Fig. 5(b), which is sufficient to feed hydrogen for a 1.5 kW fuel cell.

5. Future challenges

When a hydrogen generator is directly used to feed hydrogen for a fuel cell system, a controllable and load-response hydrogen flow rate is generally required. Hydrogen generation by the reaction of aluminum and/or aluminum-based alloys with water provides a simple, safe and cost competent way to supply hydrogen for fuel cells. Recent progress has indicated that building a direct Al-based hydrogen generator–fuel cell power system is feasible. However, difficulties to design and manufacture an on-demand generator directly for fuel cell application still remain due to its reactive nature. Aluminum is in the form of solid state and so the feeding amount of which is not easy to precisely control. The hydrogen generation reaction generally occurs at the aluminum surface and the as-formed fluffy hydrolysis byproduct would cover on the aluminum surface and consequently prevent the reaction to proceed continuously. Another factor is that according to the reaction (3), a considerable heat release is associated with the hydrolysis reaction, so without sufficient heat exchange measures an explosive reaction would generally take place, particularly when aluminum is in the form of fine particles. Therefore it is essential to solve these engineering issues before an Al-based hydrogen generator used in a practical fuel cell system becomes possible. Based on these considerations, the future work is recommended to focus on the following aspects: 1) developing highly activated

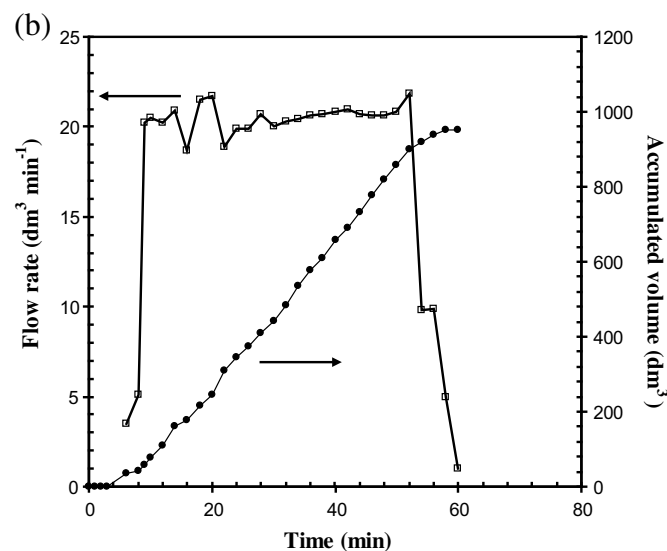
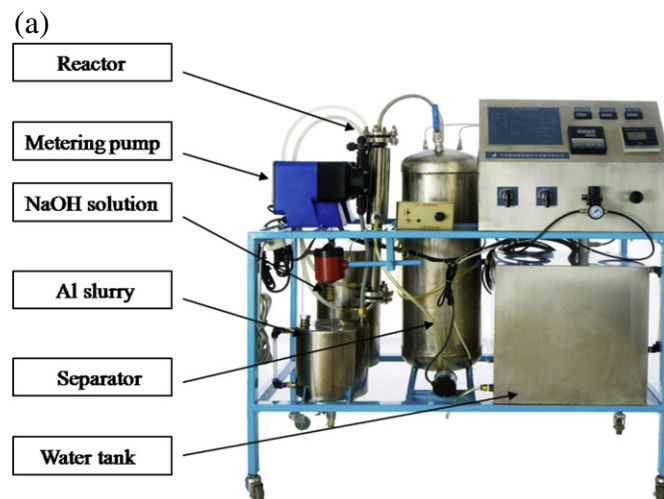


Fig. 5. (a) Diagram of hydrogen generator. By courtesy of Tianjin Highland Energy Technology Development Co., Ltd. [86]. (b) Time dependence of H₂ flow rate and accumulated volume of the prototype hydrogen generator. Taken from Ref. [85].

aluminum materials either by doping or by addition of suitable additives; 2) instant removal of hydrolysis product. The as-produced hydrolysis product $\text{Al}(\text{OH})_3$ or AlOOH are fluffy and stick, which would cover on the surface of Al particles and thus stop the hydrogen generation to progress. Therefore it is important, using suitable measures, to instantly remove $\text{Al}(\text{OH})_3$ or AlOOH to attain a continuous hydrogen generation rate; and 3) heat removal. To control the reaction and increase the safety of Al-based hydrogen generator, appropriate heat exchange measures should be taken into account.

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